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THE DETERMINATION OF RATE CONSTANTS OF ELEMENTARY REACTIONS OF HYDROGEN ATOMS

1. The Rate Constant of the Recombination $H + H + H_2 \rightarrow 2H_2$ and
That of the Reaction $H + O_2 + H_2 \rightarrow HO_2 + H_2$

L. I. Avramenko and R. V. Kolesnikova

The rate constant of the reaction of formation of the HO_2 radical
from H atoms and O_2 molecules during $H + O_2 + M \rightarrow HO_2 + M$ triple col-
lisions, where M is the H_2 molecule, was previously determined by
other authors /1-3/. The three values obtained for the constant do
not agree with each other, the minimum value /1/ differing from the
maximum /2/ by two orders. The rate constant of the recombination of
hydrogen atoms during triple collisions was also determined previously
by a number of authors /1,4-6/. The values are in good agreement with
each other. The present work was undertaken for the purpose of de-
termining the rate constants of the reaction $H + O_2 + H_2 \rightarrow HO_2 + H_2$
on the basis of a method proposed by us for determining the rate con-
stants of atoms and radicals /7/.

Experimental Part

The experiments were conducted in a stream on glass vacuum apparatus, the design of which is shown in Fig. 1. The source of hydrogen atoms was a silent discharge occurring in an ozonator-type device. For the discharge a high-voltage transformer was used at 40,000 volts. The ozonator was connected to the reaction vessel by a narrow nozzle. The nozzle between the discharge zone and the reaction vessel made it impossible for O_2 molecules to diffuse into the discharge zone during the feeding of the O_2 molecules into the stream containing the H atoms. The reaction vessel had a diameter of 20 mm and a length of 1.2 m. The electrolytic molecular hydrogen used for the experiments was stored in an ordinary balloon. The balloon was connected to the apparatus by a special valve similar to the valves used on aqualungs for underwater swimming; it enabled us to keep the hydrogen under constant atmospheric pressure. Between the valve and the glass part of the apparatus was a tube of calcium chloride for purifying the H_2 of water vapor and oil, which fly in, together with the hydrogen, from the balloon. At the end of the reaction tube was a removable trap cooled by liquid nitrogen. The stream and the vacuum were created with the aid of an oil fore pump.
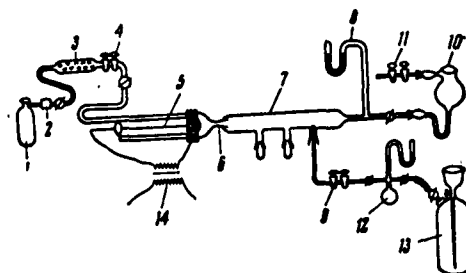

Fig. 1. Design of the apparatus: 1) balloon containing hydrogen; 2) special valve; 3) tube containing $CaCl_2$; 4,9,11) stopcock valves; 5) ozonator-type tube; 6) nozzle; 7) reaction vessel; 8) manometer for measuring the pressure in the reaction vessel; 10) removable trap; 12) calibrated vessel, from which the O_2 is fed into the reaction vessel; 13) gas meter for O_2.

In order to increase the number of hydrogen atoms drawn off into the reaction vessel, the walls of the nozzle were coated with phosphoric acid. We proceed from the assumption that the reaction of formation of HO_2 (in the interaction between H and O_2) is a trimolecular reaction. Bearing in mind that Hudson and Foner [8] did not detect HO_2 at low pressures and detected HO_2 mass-spectroscopically (in the reaction $H + O_2$) at a pressure of 20 mm, the present experiments were conducted at a pressure of 60 mm. The basic pressure in the reaction vessel was created by the hydrogen. The temperature was room temperature. The feeding of molecular oxygen into the reaction vessel led to the formation of hydrogen peroxide, which was detected in the trap cooled by liquid nitrogen after defrosting. The quantity of peroxide was determined by titration with a solution of $KMnO_4$ (0.05 N) in an acid medium. The minimum quantity of peroxide determined by this method is $3 \cdot 10^{-7}$ M. Usually after the reaction $(6 \text{ to } 7) \cdot 10^{-6}$ M H_2O_2 was detected.

Table

length of reaction vessel, cm	quantity of peroxide after 20 min, M $\cdot$ 10^6
40	5.0
120	4.8
440	5.1

Control tests (without additions of O_2) were carried out with a discharge in hydrogen at various pressures. These tests showed that hydrogen peroxide is not formed in the absence of O_2; however, we do observe the formation of water as a result of small admixtures of O_2 in the H_2. To prove that the formation of H_2O_2 under these conditions is related to the HO_2 radical was important, because in the earlier investigation carried out by the discharge-tube method at pressures of ~6 mm in the reaction $H + O_2$ we also detected hydrogen peroxide

in the reaction products /9/. However, in the case of reactions at low pressure /9/ and a temperature of $\sim 100°$ a completely different mechanism of formation of hydrogen peroxide takes place, a mechanism not involving HO_2. It was found /9/ that the basic reaction $H + O_2$ is a surface reaction leading to the formation of OH and O and not to the formation of HO_2. The formation of hydrogen peroxide occurs in this case on the cold walls of the trap cooled by liquid nitrogen. Thus, if the formation of peroxide in the present experiments were related to the presence of a surface reaction, a decrease in pressure should have facilitated the formation of H_2O_2, since diffusion of the hydrogen atom to the surface is made easier.

Low-pressure experiments were carried out, as well as experiments to determine the dependence of the output of peroxide on the length of the reaction vessel. The experiments carried out at a pressure of 10 mm, all other conditions being the same as the conditions of the experiments at 60 mm, showed the practical absence of hydrogen peroxide. The decrease in the formation of hydrogen peroxide with decreasing pressure definitely indicates the participation of a third particle (the H_2 molecule) in the mechanism of formation of H_2O_2. The results of the experiments to determine the dependence of the rate of formation of peroxide on the length of the reaction vessel are presented in the table.

The table shows that there is no relation between the rate of formation of H_2O_2 and the distance of the cold walls of the trap from the place where the H and O_2 are mixed. This means that the formation of H_2O_2 is not related to the cold walls, but occurs in the interior of the volume. The experiments carried out enable us to draw conclusions concerning the mechanism of the reaction $H + O_2$ under the con-

ditions of the experiments. The effect of the third particle attests to the fact that the main reaction is the reaction $H + O_2 + H_2 \to HO_2 + H_2$.

As a result of the fact that the formation of H_2O_2 ends more than a distance of 40 cm from the place where the H and the O_2 are mixed, when the stream velocity is 90 cm/sec, we can conclude that the HO_2 radical is converted fairly rapidly into H_2O_2 according to the reaction $2HO_2 \to H_2O_2 + O_2$.

The formation of H_2O_2 from the reaction $HO_2 + H_2 \to H_2O_2 + H_2$ is excluded as a result of the low temperature. An attempt was made by us to condense the HO_2 radical with the aid of liquid-nitrogen cooling by placing the trap at a distance of 4 cm from the mixing place of the H and the O_2. This attempt turned out to be successful. Figure 2 shows a photograph of the EPR spectrum of the frozen condensate[*]. As can be seen from Fig. 2, the signal has an asymmetrical shape; the g-factor is close to the g-factor of diphenylpicrylhydrazyl. The total width of the signal is 23-26 oersteds. The defrosting of the condensate led to the destruction of the signal. An attempt to freeze the HO_2 at a distance of 1 m from the mixing place of the H and the O_2 ended with a negative result, in accordance with the data in the table, since already at a distance of 40 cm all the HO_2 is converted into H_2O_2. The spectrum of the frozen condensate of an experiment conducted without additions of O_2 (control experiment) was recorded. In this case the signal is practically absent. Thus there is no doubt of the correctness of the proposed mechanism of the interaction between H and O_2 according to the reaction $H + O_2 + H_2 \to HO_2 + H_2$.

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[*] The EPR spectrum of the HO_2 radical was recorded by G. A. Kapralova on an IKhF-2 spectrometer.

The rate constant of the reaction $H + O_2 + H_2 \rightarrow HO_2 + H_2$ was determined by a method proposed earlier /7/. In order to determine the rate constant of the reaction $H + O_2 + H_2$, it is necessary to measure the rate of accumulation of the primary product in relation to the feeding rate of the molecular oxygen. The primary product of this reaction is the HO_2 radical, the concentration of which we do not measure directly. However, under the conditions of our experiments the HO_2 radicals are converted into peroxide as a result of the interaction between two HO_2 radicals.
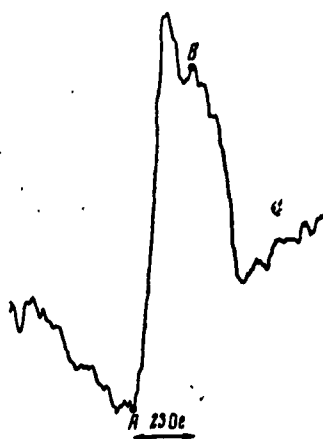

Fig. 2. EPR spectrum of the HO_2 radical at the temperature of liquid nitrogen in the solid phase frozen from the gaseous phase.

The dependence of the final concentration of the primary product $(H_2O_2)_k$ on the initial concentration of oxygen $(O_2)_0$ was derived on the basis of the following schema:

$$H + O_2 + H_2 \overset{k}{\rightarrow} HO_2 + H_2 \qquad\qquad (1)$$
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad\qquad (2)$$
$$H + H + H_2 \overset{k_H'''}{\rightarrow} 2H_2, \qquad\qquad (3)$$

where k_H''' is the rate constant of the destruction of hydrogen atoms.

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From the condition of stoichiometry the final concentration of hydrogen peroxide $(H_2O_2)_k$, measured during the experiment, can be expressed as follows:

$$(H_2O_2)_k = (O_2)_0 - (O_2)_k, \qquad (4)$$

where $(O_2)_k$ is the final concentration of molecular oxygen.

On the basis of the schema let us write the following equations:

$$\frac{d(H)}{dt} = -k(H)(O_2)(H_2) - k_{\text{к}}'''(H)^2(H_2) \qquad (5)$$

$$\frac{d(O_2)}{dt} = -k(H)(O_2)(H_2) \qquad (6)$$

Dividing (5) by (6), we obtain:

$$\frac{d(H)}{d(O_2)} = 1 + \frac{k_{\text{к}}'''(H)}{k(O_2)} \qquad (7)$$

The solution of differential equation (7) leads to the following dependence of (H) on (O_2):

$$(H) = \frac{k}{k - k_{\text{к}}'''}(O_2) + C(O_2)^{\frac{k_{\text{к}}'''}{k}}, \qquad (8)$$

where C is the constant of integration, which is determined from the boundary conditions, when $(H) = (H)_0$ and $(O_2) = (O_2)_0$, where $(H)_0$ is the initial concentration of hydrogen atoms.

Under the conditions of our experiments the concentrations of (H_2O_2) and (O_2) cease changing, i.e., they become final, when all the hydrogen atoms are used up. The correctness of this condition: $(H_2O_2) = (H_2O_2)_k$ and $(O_2) = (O_2)_k$, when $(H) = 0$, is apparent from the table, since the quantity of peroxide remains constant as the reaction zone increases in length.

Using the condition: $(O_2) = (O_2)_k$, when $(H) = 0$, and replacing $(O_2)_k$ by $(O_2)_0 - (H_2O_2)_k$ from equation (8), we obtain

$$\frac{k}{k-k_{H}'''}\,[(O_2)_0 - (H_2O_2)_K] + \left[(H)_0 - \frac{k}{k-k_{H}'''}\,(O_2)_0\right]\left[1 - \frac{(H_2O_2)_K}{(O_2)_0}\right]^{\frac{k_{H}'''}{k}} = 0$$

Since $\frac{(H_2O_2)_K}{(O_2)_0} \ll 1$, the quantity $\left[1 - \frac{(H_2O_2)_K}{(O_2)_0}\right]^{\frac{k_{H}'''}{k}}$ can be expanded in series.

Confining ourselves to the first two terms of the series, we obtain the equation

$$\frac{1}{(H_2O_2)_K} = \frac{1}{(H)_0} + \frac{k_{H}'''}{k\,(O_2)_0} \tag{9}$$

Equation (9) is the equation of a straight line in the coordinates $1/(H_2O_2)_K;\ 1/(O_2)_0$. The constant k is determined from the slope of the straight line according to the equation

$$k = \frac{k_{H}'''}{\tan \alpha} \tag{10}$$

Thus, in order to determine the constant k, it is necessary to determine the dependence of $(H_2O_2)_K$ on $(O_2)_0$ and to know the rate constant of the destruction of hydrogen atoms. It was already mentioned that there are papers dealing with the determination of the rate constant of the destruction of hydrogen atoms, wherein it was found that the destruction obeys the trimolecular law $H + H + H_2 \rightarrow H_2 + H_2$, i.e., it is quadratic. We could have used the data of other authors on the rate constant of the recombination of hydrogen atoms. However, it was important for us to determine the rate constant of the destruction of hydrogen atoms under the conditions of our experiments. In order to determine the rate constant of the destruction of hydrogen atoms, we used a method of determining the destruction rate constants of atoms and radicals published by us earlier /10/. On the basis of this method the determination of the concentration of hydrogen atoms over the length of the reaction vessel for the case of predominance

of quadratic destruction is written in the form

$$\frac{(H)_0}{(H)_x} = 1 + \frac{x k_H''' (H)_0 (H_2)}{w},$$

(11)

while in the case of predominance of linear destruction

$$\log \frac{(H)_0}{(H)_x} = \frac{k_H x}{w} 0.43,$$

(12)

where $(H)_x$ is the concentration of H atoms at a distance x; k_H is the rate constant of linear destruction of H; w is the linear velocity of the stream.

By determining the dependence of $\dfrac{(H)_0}{(H)_x}$ on x and plotting the graph, we can ascertain whether the predominant recombination of H atoms is quadratic.

If the points on the graph of the dependence of $\dfrac{(H)_0}{(H)_x}$ on x lie on a straight line, whose y-intercept is equal to 1, then quadratic recombination is predominant.

Figure 3 shows a straight line obtained from the experimental points at room temperature with p_{H_2} = 60 mm and w ≡ 90 cm/sec. The concentration of hydrogen atoms in different places in the reaction vessel along the path of the stream was determined from the maximum output of hydrogen peroxide resulting when molecular oxygen is fed into different places in the reaction vessel.
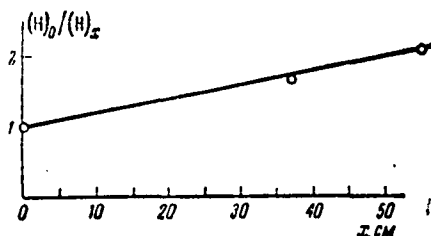

Fig. 3. The dependence of the relative concentration of hydrogen atoms $\dfrac{(H)_0}{(H)_x}$ on the distance x.
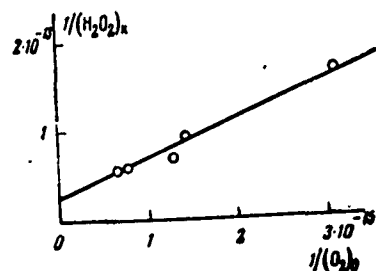
Fig. 4. The dependence of the reciprocal of the final concentration of hydrogen peroxide $1/(H_2O_2)_k$ on the reciprocal of the initial concentration of oxygen molecules $1/(O_2)_0$.

The experimental points in a large interval of values x (55 cm) fit quite well on a straight line with a y-intercept equal to unity. However, in the coordinates $\log \frac{(H)_0}{(H)_x}$; x we again obtain a straight line; only this one starts from the origin. In order to ascertain the law according to which the hydrogen atoms are destroyed, we must resort to a theoretical consideration of cases involving different ratios between the constants of linear and quadratic destruction, as was done previously /10/. In one case, where the linear destruction is small in absolute value and the quadratic destruction is 3 to 4 times greater than the linear, we obtain a straight line in the co-ordinates $\frac{(H)_0}{(H)_x}$; x, while in the coordinates $\log \frac{(H)_0}{(H)_x}$; x we obtain a curve which is close to a straight line. Our experimental data approach this case. Consequently, the predominant destruction is quadratic; therefore the quantity $k_H'''(H)_0$ must be determined from the graph in Fig. 3 according to the equation

$$k_H'''(H)_0 = \frac{w \tan \beta}{(H_2)}$$

(13)

The following value was obtained for this quantity:

$$k_H'''(H)_0 = 9 \cdot 10^{-19} \; cm^3 \cdot sec^{-1} \cdot molecules^{-1}$$

In the determination of the dependence of $\frac{(H)_0}{(H)_x}$ on x the initial concentration of hydrogen atoms $(H)_0$ had a value equal to $1.72 \cdot 10^{13}$ molecules/cm^3. Hence $k_H''' = 5.2 \cdot 10^{-32} \; cm^6 \cdot sec^{-1} \cdot molecules^{-2}$.

The value obtained for k_H''' is in good agreement with the values for this quantity given by other authors: according to Farkas and Sachsse /1/ $k_H''' = 9.3 \cdot 10^{-32}$, according to Smallwood /4/ $4.65 \cdot 10^{-32}$, according to Steiner /5/ $3.5 \cdot 10^{-32}$, according to Amdur /6/ $3.3 \cdot 10^{-32}$ (in $cm^6 \cdot sec^{-1} \cdot molecules^{-2}$).

In order to determine the rate constant of the reaction $H + O_2 +$ $+ H_2 \rightarrow HO_2 + H_2$, we determined the dependence of $(H_2O_2)_k$ on $(O_2)_0$. Figure 4 shows the experimental data for room temperature with $P_{H_2} =$ $= 60$ mm and $w = 90$ m/sec. From the slope of the straight line (Fig. 4) and the value $k_H'' = 5.2 \cdot 10^{-32}$ the value of the trimolecular rate constant of the reaction $H + O_2 + H_2 \rightarrow HO_2 + H_2$ was obtained according to formula (10).

$$k = 1.2 \cdot 10^{-33} \text{ cm}^6 \cdot \text{sec}^{-1} \cdot \text{molecules}^{-2}$$

The value of this constant agrees with the data of Nalbandyan and Voyevodskiy /3/ $(2.4 \cdot 10^{-33})$, is one order of magnitude greater than the data of Farkas and Sachsse /1/, and is an order of magnitude less than the data of Cook and Bates /2/.

In conclusion, the authors express their thanks to G. A. Kapralova for recording the EPR spectrum of the HO_2 radical.

Conclusions

1. The rate constant of the trimolecular process of formation of HO_2 in the reaction between hydrogen atoms and O_2 molecules at room temperature was determined.

2. The rate constant of recombination of hydrogen atoms during triple collisions was determined.

3. The EPR spectrum of the HO_2 radical frozen from the gaseous phase was recorded at the temperature of liquid nitrogen.

4. The great capacity of the HO_2 radical to be converted into H_2O_2 was detected

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